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GENERAL METHOD OF DETERMINING COMPOSITION AND MOLECULAR STRUCTURE
 OF A CHEMICAL COMPOUND OF ELEMENTS PRESENT IN RADIOCHEMICAL,
 i.e., UNWEIGHABLE QUANTITIES

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[This article presents a summary of Khlopin's discoveries in the theoretical field. The actual work to which the relationships in question apply is concerned with the isolation, concentration, and purification of radioactive elements from the practical standpoint.]

Mitscherlich's law of isomorphism, discovered about 1820, states that two chemical compounds are isomorphous if they have similar chemical composition and molecular structure, in which case they may form mixed or isomorphous crystals when crystallizing. In fact, until the 1890's, this law served as a reliable means of checking the chemical composition and molecular structure of chemical compounds which had been established by chemical analysis. If this law has been used repeatedly to establish the chemical composition and molecular structure of chemical compounds, then why is it necessary to consider this question again as regards radiochemical quantities of substances?

The point is that at the present time, after the development of crystallochemistry and the work of Grimm (1), Goldschmidt (2), and their associates and followers, the concept of isomorphism has become much more complex, and we distinguish between isomorphism of the first, second, and third kind. While Mitscherlich's law has remained valid for isomorphism of the first order, it does not apply to isomorphism of the second or third kind. Therefore, at present, the possibility of using Mitscherlich's law for determining the chemical composition and molecular structure of chemical compounds is limited by the absence of a method which would allow distinguishing reliably between isomorphism of the first kind and the other cases of isomorphism. Until our work on the

- 1 -

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50X1-HUM

study of the distribution of microcomponents between the solid crystalline phase and the solution, such a method did not exist, and even the most exact method for determining crystalline structure, X-ray analysis, did not disclose any difference between mixed crystals formed by two compounds, isomorphous according to the first type, and mixed crystals formed by two compounds, isomorphous according to the second or third type. In all cases where mixed crystals are formed, a change in the permanent lattice was observed, according to Vegard's [?] law, which was considered a certain indication of isomorphic change.

Matters remained that way until 1929, when I, in cooperation with B. A. Nikitin (3), was the first to show, by using radioactive elements as indicators in determining the possibility of formation and the structure of mixed crystals of Grimm's new type (isomorphism of the second kind), that these mixed crystals are fundamentally different from the mixed crystals formed by substances, isomorphous according to Mitscherlich's law (isomorphism of the first kind).

The fundamental distinction between the true isomorphous mixed crystals, as we shall now call mixed crystals, which are formed from substances isomorphous according to the first kind of isomorphism (isomorphism according to Goldschmidt), and isomorphism of the second and third kind (according to Goldschmidt's classification) consists of the following: in the joint crystallization of two substances which are true isomorphs, mixed crystals will always form, however low the concentration of one of the crystallizing substances might be, as long as the concentration of the solution in regard to the second substance is sufficient for the latter to start crystallizing.

Conversely, in the case of isomorphism of the second or the third kind, a lower limit of miscibility is always observed (3, 4), i.e., formation of mixed crystals will not take place at all, if the concentration in the solution of one of the substances is lower than the concentration corresponding to the lower limit of miscibility. The concentration corresponding to the lower limit of miscibility should depend on the degree of complexity of the elementary crystal nuclei of the crystallizing substances; it is to be expected that this concentration will be the greater, the more complex the elementary crystalline nucleus of the crystallizing substance, i.e., the greater the number of particles required for its construction.

Thus, the essential difference between true isomorphism and all other cases of apparent isomorphism can be established relatively easily, not by investigation of the finished mixed crystals in their static condition, as is usually done, but in the dynamics, by investigation of the properties or the mechanism of the formation of mixed crystals during joint crystallization of two substances from solution. I explain the difference by assuming that in a joint crystallization of true isomorphs, to which Mitscherlich's law is applicable, during the formation of mixed crystals, a replacement of one compound in the lattice by the other compound takes place, ion by ion, atom by atom, or molecule by molecule, depending on the type of the lattice.

In all other cases of joint crystallization, a much more complex replacement process takes place in the formation of mixed crystals, viz., in the case of isomorphism of the second and third kind, replacement takes place by exchange of finished elementary crystal cells of both crystallizing substances, while in the case of formation of typical anomalous mixed crystals, replacement involves even larger regions of complete crystalline lattices of both crystallizing substances. My students and I succeeded in showing without doubt that the law of distribution of substances between two immiscible solvents applies strictly only in the case of distribution between the solid crystalline and the liquid phase of true isomorphous substances (4-8).

- 2 -

S-E-C-R-E-T**SECRET**

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50X1-HUM

We recall that under strict application of the law of the distribution of substances between two immiscible solvents, the coefficient of crystallization or the constant of distribution $K_{\phi}(D)$ should not depend on the concentration of the substance being distributed, as long as that concentration does not become greater than 0.005 molar, i.e., as long as the presence of the microcomponent does not have any effect on the composition of the phases.

We can now formulate the following rule: if the distribution of a microcomponent (radioactive element) between the solid crystalline phase and the solution proceeds strictly according to the law of the distribution of substances between two immiscible solvents, and if the coefficient of crystallization $K_{\phi}(D)$ remains at a constant magnitude during change within a wide range (by several orders of magnitude) of the concentration of the substances being distributed, then this can serve as an indication that Mitscherlich's law can be extended to the given pair of substances, i.e., the conclusion can be drawn that the chemical composition and molecular structure of the macro- and microcomponent are analogous.

This rule allows making use of the investigation of the distribution of microcomponents between the solid crystalline phase and the solution and of Mitscherlich's law in the chemistry of radioactive elements, i.e., in the entire field of the chemistry of carriers, for the determination of the chemical composition of compounds and of their molecular structure, in the case of natural and artificial radioactive elements which we cannot have in weighable quantities and which do not have stable isotopes, i.e., in all those cases where chemical analysis cannot be applied for these reasons.

The author made use of this rule for the first time in 1934 in his joint work with A. G. Samartseva, proving the bivalency of polonium in derivatives of polonium hydride. Later, B. A. Nikitin used this rule in his discovery of hydrates and other molecular compounds of radon in connection with which he brought the conclusive proof that the law of distribution of a substance between two immiscible solvents is applicable also in the case of distribution of a microcomponent between the solid crystalline and gaseous phase in the joint crystallization of a microcomponent and a macrocomponent from the gaseous phase. In general, from 1934 on, both B. A. Nikitin and the students and associates of the author have been repeatedly and successfully using this rule without referring to it as such. We therefore consider it absolutely necessary to publish this rule, although somewhat belatedly, at the present time, when the chemistry of carriers has attained such development and importance.

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- 3 -

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50X1-HUM

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- 4 -

S-E-C-R-E-T

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